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A TANDEM ESTER CLEAVAGE-MICHAEL ADDITION REACTION FOR THE SYNTHESIS OF OXYGEN HETEROCYCLES

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Abstract: A tandem ester cleavage-Michael addition sequence has been developed for the preparation of five- and six-ring oxygen heterocycles bearing an acetic acid residue at C-2. Treatment of ethyl 6- or 7-acetyloxy-2-alkenoates with ethanolic sodium ethoxide affords the tetrahydrofuran and tetrahydropyran products in 70-90% yields. The reaction is clean and appears to be a general route for the preparation of these compounds. Steric hindrance to the initial acetate cleavage and unfavorable entropy in closing large rings appear to be the only limitations to the procedure.

Introduction. Five- and six-membered ring heterocycles are attractive intermediates for the synthesis of natural products and medicinal agents. We recently reported[2] a tandem S_N2-Michael reaction for the synthesis of five- and six-membered nitrogen and sulfur heterocycles and we sought a method for applying this or similar technology to the synthesis of oxygen heterocycles. In contrast to our previous study, initiation of the heterocyclization process by direct S_N2 displacement of a halogen would prove difficult due to competing elimination by the more basic oxygen nucleophile. We have, therefore, explored the use of 6- and 7-acetyloxy-2-alkenoates as our cyclization substrates and describe here our results on the synthesis of tetrahydrofuran- and 2*H*-tetrahydropyran-2-acetates using an ester cleavage-Michael addition reaction.

The preparation of oxygen heterocycles by intramolecular Michael addition of alkoxides to unsaturated esters has been previously reported[3,4] in the synthesis of several biologically active compounds. Similar cyclizations have been described in

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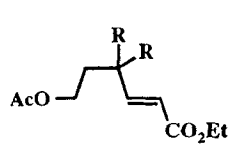
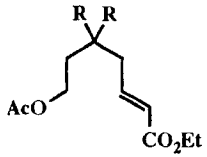
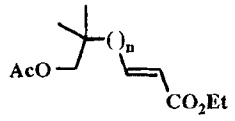


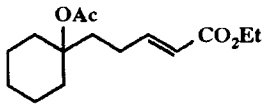
11 (R,R = H)
12 (R,R = Me)
13 (R,R = -(CH2)5-)



14 (R,R = H)
15 (R,R = Me)



16 (n = 1)
17 (n = 2)



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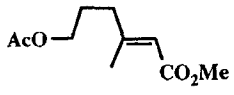
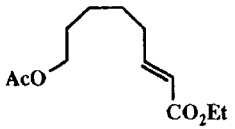


19

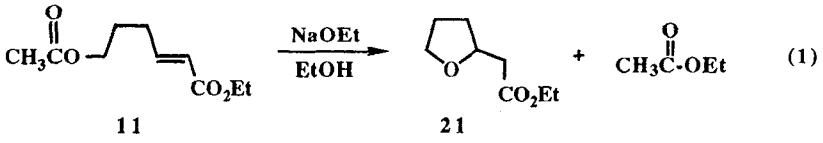


20

systems incorporating unsaturated ketones,[5] aldehydes,[6] acids[7] and nitriles[8] and also as part of other tandem processes.[9] These cases have established the feasibility and utility of the process but have not explored the steric requirements of the reaction or the substitution patterns accessible.

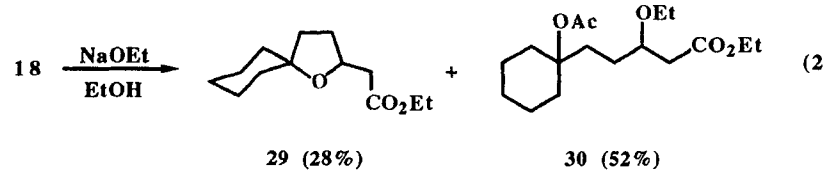
Preparation of Starting Materials: Cyclization substrates **11-18** were easily prepared from commercial 4-pentenyl acetate (**1**) and 5-hexenyl acetate (**4**) as well as acetates **2**, **3**, **5**, **6**, **7** and **8** which were readily derived from the known[10] alcohols. Ozonolysis of the acetyloxy alkenes and treatment of the resulting aldehydes with ethyl (triphenylphosphoranylidene)acetate[11] afforded the required ω-acetyloxy-2-alkenoates (**11-18**) in 45-70% yields. Methyl (*E*)-6-acetyloxy-3-methyl-2-hexenoate (**19**) was prepared in 43% yield from 5-acetyloxy-2-pentanone (**9**)[12] by treatment with the trimethyl phosphonoacetate anion.[13] Finally, ethyl (*E*)-8-acetyloxy-2-octenoate (**20**) was prepared in 61% yield from 6-acetyloxy-1-hexanol (**10**)[14] by sequential oxidation with buffered PCC[15] followed by treatment with the stabilized ylide.

Results and Discussion: The ring closure (eq 1) was effected by treatment of the acetyloxy alkenoates with ethanolic sodium ethoxide (substrates **11-17**) or methanolic sodium methoxide (substrate **19**) at room temperature for 8-12 h. Ammonium chloride workup afforded the tetrahydrofuran and tetrahydropyran derivatives in yields of 70-90%. The ethyl (or methyl) acetate by-product was easily removed during concentration of the final product. The products isolated from this process were pure enough for most purposes; PTLC or vacuum distillation afforded material suitable for analysis. Our results are summarized in Table 1.

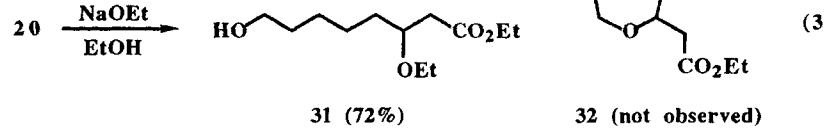


11 21 (1)

The reaction appears to proceed equally well for both five- and six-membered ring closures. Evaluation of a range of substrates revealed that the reaction is limited by steric hindrance to acetate cleavage and the size of the ring being closed. Attempted cyclization of ethyl (*E*)-5-(1-acetoxycyclohexyl)-2-pentenoate (**18**) established the importance of the steric environment around the acetate. Treatment of this substrate with ethanolic sodium ethoxide under the standard conditions yielded a complex mixture containing 28% (GC) of the cyclization product **29** and 52% (GC) of product **30** derived from Michael addition of ethoxide to the acrylate moiety (see eq 2). Steric hindrance surrounding the Michael acceptor, as in substrates **12**, **13** and **19**, did not adversely affect the final Michael addition. A seven-ring closure was also attempted on ethyl (*E*)-8-acetyloxy-2-octenoate (**20**)



29 (28%) 30 (52%) (2)

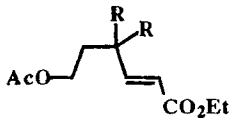
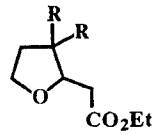
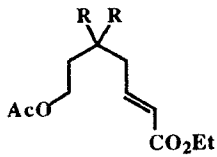
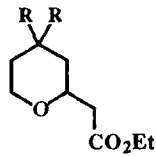
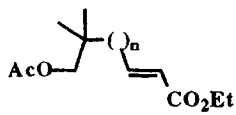
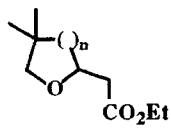
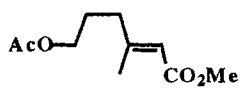
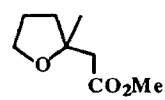


31 (72%) 32 (not observed) (3)

but the predominant product (72% using 2.2 eq of base) was ethyl 3-ethoxy-8-hydroxyoctanoate (**31**); none of the oxepane derivative **32** was observed (see eq 3). Thus, beyond six-ring closures, entropy disfavors intramolecular cyclization and allows intermolecular addition of ethoxide to successfully compete.

The mechanism of the oxygen heterocyclization begins with addition of ethoxide to the acetate carbonyl. Collapse of the resulting tetrahedral intermediate then produces a molecule of ethyl acetate and an ω-alkoxy-2-alkenoate which

Table 1. Oxygen Heterocycles by Tandem Ester Cleavage-Michael Addition

Starting Acetate	Oxygen Heterocycle	Yield (%)[a]
		
11 (R,R = H)	**21**	**74**
12 (R,R = Me)	**22**	**79**
13 (R,R = -(CH$_2$)$_5$-)	**23**	**80**
		
14 (R,R = H)	**24**	**84**
15 (R,R = Me)	**25**	**82**
		
16 (n = 1)	**26**	**70**
17 (n = 2)	**27**	**85**
		
19	**28**	**90**

[a]Yields refer to isolated purified products.

cyclizes by a favorable five-exo-trig or six-exo-trig[16] Michael addition process. Since alkoxide exchange of the ethyl ester consumes none of the base and has no overall effect on the substrate, the reaction proceeds cleanly using only a slight excess (1.2 eq) of base. The ethyl acetate formed as a by-product in the reaction is easily removed under aspirator vacuum during concentration of the product.

The tandem ester cleavage-Michael addition reaction constitutes an efficient approach to the synthesis of substituted five- and six-membered oxygen heterocycles bearing an acetic acid residue at C-2. The ease and versatility of the process make it a valuable addition to the synthetic methodology[17-29] currently available for the preparation of these systems. Further efforts are underway to expand the number of accessible heterocycles using this approach and to apply this technology to the synthesis of several biologically active natural and unnatural compounds.

Experimental Section

General Considerations. All reactions were run under dry N_2. THF was distilled from $LiAlH_4$ prior to use; all other solvents and reagents were used as received from the vendors. The starting acetates and alcohols were obtained from the following sources: 4-pentenyl acetate (**1**) and 5-hexenyl acetate (**4**) (Wiley Organics); 3-acetyl-1-propanol (Aldrich); 3,3-dimethyl-4-penten-1-ol,[10] 3,3-dimethyl-5-hexen-1-ol,[10] 2-(1-ethenylcyclohexyl)ethanol,[10] ethyl (triphenylphosphoranylidene)acetate,[11] 5-acetyloxy-2-pentanone[12] and 6-acetyloxy-1-hexanol[14] were prepared by literature methods. Unless otherwise indicated, the NH_4Cl, $NaHCO_3$, 1*M* HCl and NaCl used in workup procedures refer to aqueous solutions. Reactions were monitored by one of the following methods: 1) TLC on hard layer silica gel GF plates (Analtech) with UV or phosphomolybdic acid detection or 2) capillary GC with FI detection (SE-30 column, 6 m x 0.25 mm i.d., 0.25 μ film thickness) programmed between 40-150°C. Preparative separations were performed by PTLC on 20 cm x 20 cm silica gel GF plates (Analtech) or by flash vacuum chromatography[30] on a 10 cm x 10 cm plug of silica gel (Grace, grade 62, 60-200 mesh). Melting points are uncorrected. IR spectra are referenced to polystyrene. ^1H NMR and ^{13}C NMR spectra were measured at 300 MHz and 75 MHz, respectively. HRMS (EI/DP) were obtained at 70 eV. Elemental analyses are ± 0.5%.

General Procedure for Conversion of Alcohols to Acetate Esters. To a 250-mL CH_2Cl_2 solution of 100 mmol of the alcohol and 200 mmol of pyridine was added 100 mg of DMAP followed by a 50-mL CH_2Cl_2 solution of 130 mmol of acetyl chloride. The mixture was stirred for 6 h at 20°C, then poured into water. The organic layer was separated and washed with 1*M* HCl, water, $NaHCO_3$, NaCl, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting product was distilled under vacuum to afford the pure acetate as a colorless oil. The following compounds were prepared:

1-Acetyloxy-3,3-dimethyl-4-pentene (2): 92%; bp 58-60°C (8 mm Hg); IR (thin film) 3080, 1742, 1640, 1370, 1240, 1038, 998, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.77 (dd, 1 H, J = 16.7, 10.8 Hz), 4.95 (d, 1 H, J = 10.8 Hz), 4.93 (d, 1 H, J = 16.7 Hz), 4.05 (t, 2 H, J = 7.5 Hz), 2.02 (s, 3 H), 1.65 (t, 2 H, J = 7.5 Hz), 1.04 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 147.1, 111.0, 61.9, 40.3, 35.5, 26.9, 21.0; HRMS *m/e* for $C_9H_{16}O$ (M^+-CH_3CO): calcd 113.0966, found 113.0954.

1-Acetyloxy-2-(1-ethenylcyclohexyl)ethane (3): 95%; bp 56-59°C (0.5 mmHg); IR (thin film) 3080, 1748, 1640, 1370, 1245, 1038, 975, 916 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63 (dd, 1 H, J = 17.7, 10.9 Hz), 5.11 (d, 1 H, J = 10.9 Hz), 4.97 (d, 1 H, J = 17.7 Hz), 4.04 (t, 2 H, J = 7.6 Hz), 2.02 (s, 3 H), 1.65 (t, 2 H, J = 7.6 Hz), 1.60-1.30 (complex, 10 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 145.3, 113.3, 61.4, 38.6, 35.6 (2), 26.3, 21.9, 21.0; HRMS *m/e* for $C_{12}H_{20}O_2$: calcd 196.1463, found 196.1463.

1-Acetyloxy-3,3-dimethyl-5-hexene (5): 87%; bp 91-92°C (35 mm Hg); IR (thin film) 3080, 1745, 1642, 1370, 1240, 1038, 998, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (ddt, 1 H, J = 16.7, 10.3, 7.5 Hz), 5.04 (m, 2 H), 4.12 (t, 2 H, J = 7.6 Hz), 2.03 (s, 3 H), 1.98 (d, 2 H, J = 7.5 Hz), 1.56 (t, 2 H, J = 7.6 Hz), 0.92 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 134.9, 117.2, 61.6, 46.7, 39.4, 32.4, 27.0, 21.0; HRMS *m/e* for $C_{10}H_{18}O_2$: calcd 170.1307, found 170.1306.

1-Acetyloxy-2,2-dimethyl-4-pentene (6): 89%; bp 44-47°C (5 mm Hg); IR (thin film) 3080, 1745, 1640, 1377, 998, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (ddt, 1 H, J = 16.7, 10.3, 7.4 Hz), 5.04 (m, 2 H), 3.79 (s, 2 H), 2.07 (s, 3 H), 2.03 (d, 2 H, J = 7.4 Hz), 0.92 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.1, 134.3, 117.6, 72.0, 43.4, 33.9, 24.0, 20.8; HRMS *m/e* for $C_9H_{16}O_2$: calcd 156.1150, found 156.1146.

1-Acetyloxy-2,2-dimethyl-5-hexene (7): 89%; bp 58-60°C (5 mmHg); IR (thin film) 3080, 1746, 1648, 1380, 995, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (ddt, 1 H, J = 16.9, 10.3, 7.3 Hz), 5.01 (d, 1 H, J = 16.9 Hz), 4.93 (d, 1 H, J = 10.3 Hz), 3.80 (s, 2 H), 2.06 (s, 3 H), 2.02 (m, 2 H), 1.35 (m, 2 H), 0.92 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.1, 139.1, 114.1, 72.3, 38.2, 33.6, 28.2, 24.1, 20.8; HRMS *m/e* for $C_{10}H_{18}O_2$: calcd 170.1307, found 170.1303.

1-Acetyloxy-1-(3-butenyl)cyclohexane (8): 68%; bp 82-83°C (12 mmHg); IR (thin film) 3080, 1745, 1652, 1375, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (ddt, 1 H, J = 17.1, 10.2. 7.3 Hz), 4.96 (d, 1 H, J = 17.1 Hz), 4.93 (d, 1 H, J = 9.2 Hz), 2.20 (m, 2 H), 2.01 (s, 3 H), 1.98 (m, 4 H), 1.62-1.42 (complex, 5 H), 1.39-1.23 (complex, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.2, 138.5, 114.3, 83.6, 36.6, 34.5, 27.5, 25.5, 22.2, 21.8; HRMS *m/e* for $C_{12}H_{20}O_2$: calcd 196.1463, found 196.1457.

General Procedure for Conversion of 5- and 6-Acetyloxyalkenes to (*E*)-6- and (*E*)-7-Acetyloxy-2-alkenoate Esters. A 350-mL CH_2Cl_2 solution of 40.0 mmol of the acetyloxy alkene at -78°C was treated with ozone until the solution turned a light blue color. The reactions were quenched at -78°C with 4.97 g (5.88 mL, 80.0 mmol) of dimethyl sulfide, warmed to 20°C and stirred for 4-6 h. The solvent was removed *in vacuo* and the crude aldehyde was used without purification.

The crude acetyloxy aldehydes were dissolved in 200 mL of benzene, then treated with 20.0 g (57.4 mmol) of ethyl (triphenylphosphoranylidene)acetate[11] and refluxed for 12 h. The reaction was cooled and concentrated *in vacuo* to afford a tan to yellow semisolid mass. The residue was added to a pad of silica gel in a 10

cm x 10 cm frit and purified by flash vacuum chromatography[30] using 2 L of 15% ether in hexane. The solvent was removed by rotary evaporation under aspirator vacuum and the resulting oil was diluted with ether, washed with water, $NaHCO_3$, NaCl, dried ($MgSO_4$) and concentrated *in vacuo*. [Note: At this point, it was found that the hindered aldehydes derived from **2** and **3** required a second treatment with 20.0 g (57.4 mmol) of the ylide.] Final purification by short path vacuum distillation afforded the following products:

Ethyl (*E*)-6-Acetyloxy-2-hexenoate (11): 4.02 g (18.0 mmol, 50%); scale-up (4x) gave 17.4 g (87.0 mmol, 54%); bp 83-86°C (0.5 mmHg); IR (thin film) 1740, 1720, 1652, 1370, 1240, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (dt, 1 H, J = 15.6, 7.0 Hz), 5.85 (d, 1 H, J = 15.6 Hz), 4.19 (q, 2 H, J = 7.0 Hz), 4.09 (t, 2 H, J = 6.5 Hz), 2.29 (q, 2 H, J = 6.5 Hz), 2.05 (s, 3 H), 1.81 (quintet, J = 6.5 Hz), 1.29 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 170.7, 166.1, 147.3, 121.8, 63.3, 59.9, 28.4, 26.8, 20.6, 14.0; HRMS *m/e* for $C_{10}H_{16}O_4$: calcd 200.1049, found 200.1045. Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 59.87; H, 7.99.

Ethyl (*E*)-6-Acetyloxy-4,4-dimethyl-2-hexenoate (12): 4.37 g (19.2 mmol, 48%); bp 93-95°C (0.5 mmHg); IR (thin film) 1742, 1720, 1650, 1370, 1240, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.93 (d, 1 H, J = 15.8 Hz), 5.74 (d, 1 H, J = 15.8 Hz), 4.19 (q, 2 H, J = 7.2 Hz), 4.05 (t, 2 H, J = 7.1 Hz), 2.01 (s, 3 H), 1.75 (t, 2 H, J = 7.1 Hz), 1.30 (t, 3 H, J = 7.2 Hz), 1.11 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.8, 166.7, 156.6, 118.0, 61.2, 60.1, 40.1, 35.6, 26.4, 20.8, 14.1; HRMS *m/e* for $C_{12}H_{20}O_4$: calcd 228.1361, found 228.1360. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 62.95; H, 8.75.

Ethyl (*E*)-3-[1-(2-Acetyloxyethyl)cyclohexyl]-2-propenoate (13): 4.88 g (18.2 mmol, 45.5%); bp 118-121°C (0.5 mmHg); IR (thin film) 1742, 1720, 1650, 1370, 1240, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.84 (d, 1 H, J = 16.2 Hz), 5.77 (d, 1 H, J = 16.2 Hz), 4.19 (q, 2 H, J = 7.2 Hz), 4.02 (t, 2 H, J = 7.3 Hz), 2.01 (s, 3 H), 1.75 (t, 2 H, J = 7.3 Hz), 1.66-1.36 (complex, 10 H), 1.30 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.8, 155.8, 120.1, 60.8, 60.3, 39.0, 38.4, 35.4, 26.0, 21.9, 20.9, 14.2; HRMS *m/e* for $C_{15}H_{24}O_4$: calcd 268.1674, found 268.1674. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 8.96. Found: C, 67.33; H, 9.08.

Ethyl (*E*)-7-Acetyloxy-2-heptenoate (14): 4.32 g (20.2 mmol, 50.5%); scale-up (4x) gave 18.8 g (87.8 mmol, 55%); bp 94-96°C (0.5 mmHg); IR (thin film) 1740, 1722, 1658, 1370, 1245, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.94 (dt, 1 H, J = 15.6, 7.0 Hz), 5.83 (dt, 1 H, J = 15.6 Hz, 1.5 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 4.07 (t, 2 H, J = 6.4 Hz), 2.24 (dq, 2 H, J = 7.1, 1.5 Hz), 2.05 (s, 3 H), 1.66 (m, 2 H), 1.55 (m, 2 H), 1.29 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.4, 148.3, 121.7, 63.9, 60.1, 31.5, 28.0, 24.3, 20.8, 14.1; HRMS *m/e* for $C_{11}H_{18}O_4$: calcd 214.1205, found 214.1205. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.68; H, 8.41. Found: C, 61.42; H, 8.38.

Ethyl (*E*)-7-Acetyloxy-5,5-dimethyl-2-heptenoate (15): 7.30 g (30.2 mmol, 75.5%); bp 113-115°C (0.75 mmHg); IR (thin film) 1745, 1725, 1650, 1370, 1240, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (dt, 1 H, J = 15.5, 7.8 Hz), 5.83 (d, 1 H, J = 15.5 Hz), 4.19 (q, 2 H, J = 7.1 Hz), 4.12 (t, 2 H, J = 6.7 Hz), 2.14 (d, 2 H, J = 7.8 Hz), 2.04 (s, 3 H), 1.60 (t, 2 H, J = 6.7 Hz), 1.30 (t, 3 H, J = 7.1 Hz), 0.97 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.1, 145.4, 123.8, 61.2, 60.0, 44.9, 39.5, 33.0, 27.0, 20.9, 14.1; HRMS *m/e* for $C_{13}H_{22}O_4$: calcd 242.1518, found 242.1514. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.46; H, 9.09. Found: C, 64.31; H, 8.98.

Ethyl (*E*)-6-Acetyloxy-5,5-dimethyl-2-hexenoate (16): 4.78 g (21.0 mmol, 52%), bp 92-93°C (0.5 mmHg); IR (thin film) 1735, 1655, 1380, 1370, 1240, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (dt, 1 H, J = 15.4, 8.0 Hz), 5.83 (d, 1 H, J = 15.4 Hz), 4.19 (q, 2 H, J = 7.2 Hz), 3.81 (s, 2 H), 2.18 (d, 2 H, J = 8.0 Hz), 2.08 (s, 3 H), 1.29 (t, 3 H, J = 7.2 Hz), 0.97 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.1, 144.9, 123.9, 71.8, 60.1, 41.7, 34.5, 24.2, 20.7, 14.2; HRMS *m/e* for $C_{12}H_{20}O_4$: calcd 228.1361, found 228.1359. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 63.02; H, 8.65.

Ethyl (*E*)-7-Acetyloxy-6,6-dimethyl-2-heptenoate (17): 5.45 g (22.5 mmol, 56%); bp 112-113 (0.7 mmHg); IR (thin film) 1745, 1730, 1660, 1380, 1375, 1245, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (dt, 1 H, J = 15.6, 6.9 Hz), 5.82 (dd, 1 H, J = 15.6, 1.5 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 3.80 (s, 2 H), 2.16 (m, 2 H), 2.07 (s, 3 H), 1.43 (m, 2 H), 1.29 (t, 3 H, J = 7.1 Hz), 0.94 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.5, 149.1, 121.1, 71.9, 60.1, 37.1, 33.6, 26.8, 24.0, 20.8, 14.2; HRMS *m/e* for $C_{13}H_{22}O_4$: calcd 242.1518, found 242.1511. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.46; H, 9.09. Found C, 64.19; H, 9.02.

Ethyl (*E*)-5-(1-Acetyloxycyclohexyl)-2-pentenoate (18): 5.79 g (21.6 mmol, 54%); bp 113-115°C (0.5 mmHg); IR (thin film) 1738, 1652, 1370, 1275, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (dt, 1 H, J = 15.6, 6.8 Hz), 5.82 (d, 1 H, J = 15.6 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 2.12 (m, 4 H), 2.03 (m, 2 H), 2.02 (s, 3 H), 1.63-1.43 (complex, 5 H), 1.42-1.25 (complex, 3 H), 1.28 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3, 166.5, 148.6, 121.5, 83.2, 60.1, 35.6, 34.4, 26.0, 25.4, 22.1, 21.7, 14.2; HRMS *m/e* for $C_{15}H_{24}O_4$: calcd 268.1674, found 268.1664. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 8.96. Found: C, 67.38; H, 9.13.

Methyl (*E*)-6-Acetyloxy-3-methyl-2-hexenoate (19). The general procedure of Balsevich[13] was applied to 5-acetyloxy-2-pentanone (**9**).[12] Sodium hydride (3.92 g of a 60% mineral oil dispersion, 98.0 mmol) was washed with pentane (3x), dried under vacuum and suspended in 150 mL of dry THF. The mixture was cooled to 0°C and a solution of 18.1 g (99.0 mmol) of trimethyl phosphonoacetate in 30 mL of dry DMSO was added dropwise during 20 min. The mixture was stirred at 0°C for 30 min and 12.5 g (86.8 mmol) of **9** in 20 mL of dry THF was added during 20 min. The reaction was warmed to 20°C and stirred for 20 h, then diluted with 200 mL of pentane and washed with $NaHCO_3$ (5x). The combined aqueous layer was back-extracted with 100 mL of pentane (1x). The combined organic phase was dried (Na_2SO_4), the solvent removed *in vacuo* and the residue was vacuum distilled (0.5 mmHg) through a 30-cm jacketed Vigreux column (1.75 cm i.d.) to afford the following: fraction 1, bp 57-60°C, 2.1 g of a 1:2 *E*:*Z* mixture; fraction 2, bp 61-65°C, 0.4 g of a 1:1 *E*:*Z* mixture; fraction 3, bp 66-70°C, 0.75 g of a 2:1 *E*:*Z* mixture; fraction 4, bp 71-74°C, 7.40 g (37 mmol, 43%) of a 19:1 mixture of *E* and Z methyl 6-acetyloxy-3-methyl-2-hexenoate. The *E* isomer gave the following spectral data: IR (thin film) 1750, 1725, 1650, 1370, 1240, 1155, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.69 (s, 1 H), 4.07 (t, 2 H, J = 6.5 Hz), 3.69 (s, 3 H), 2.23 (t, 2 H, J = 7.5 Hz), 2.17 (s, 3 H), 1.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 170.9, 166.7, 158.6, 63.5, 50.7, 37.0, 26.2, 20.8, 18.5; HRMS *m/e* for $C_{10}H_{16}O_4$: calcd 200.1049, found 200.1047. Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 59.95; H, 8.01.

Ethyl (*E*)-8-Acetyloxy-2-octenoate (20). A 50-mL CH_2Cl_2 solution of 10.0 g (62.5 mmol) of 6-acetyloxy-1-hexanol[14] was added dropwise to a 0°C mechanically stirred suspension of 33.6 g (156 mmol) of PCC and 1.98 g (24.0

mmol) of anhydrous NaOAc in 250 mL of CH_2Cl_2.[15] The reaction was warmed to 20°C and stirred for 3 h. The mixture was diluted with 200 mL of pentane, filtered through Celite® and concentrated to give 9.8 g of the crude aldehyde which was used without further purification.

The acetyloxy aldehyde was treated with 25.0 g (71.8 mmol) of ethyl (triphenylphosphoranylidene)acetate[11] as described above. The product was short path vacuum distilled to afford 8.68 g (38.1 mmol, 61%) of **20** as a colorless oil, bp 115-116°C (0.5 mmHg). IR (thin film) 1742, 1725, 1660, 1370, 1245, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (dt, 1 H, J = 15.6, 6.9 Hz), 5.82 (d, 1 H, J = 15.6 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 4.05 (t, 2 H, J = 6.6 Hz), 2.22 (m, 2 H), 2.04 (s, 3 H), 1.64 (m, 2 H), 1.50 (m, 2 H), 1.28 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.5, 148.6, 121.4, 64.1, 60.0, 31.8, 28.2, 27.5, 25.3, 20.8, 14.1; HRMS *m/e* for $C_{12}H_{20}O_4$: calcd 228.1361, found 228.1360. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 63.03; H, 8.76.

General Procedure for Oxygen Heterocyclizations with Ethanolic Sodium Ethoxide. Ethanolic NaOEt was prepared on a 6.00 mmol scale by dissolving 0.14 g (6.00 mg-atm) of sodium metal in 5 mL of abs EtOH. To this mixture was added a 5-mL abs EtOH solution of 5.00 mmol of the acetyloxy alkenoate ester dropwise during 5 min. The reaction was stirred for 8 h, then poured into 100 mL of NH_4Cl and extracted with ether (2x). The ether layer was washed with NaCl, dried ($MgSO_4$) and concentrated *in vacuo*. For substrate **19**, methanolic NaOMe was used for the cyclization. The products isolated were pure by NMR; samples for analysis were obtained by PTLC using 50% ether in hexane. The following compounds were prepared:

(±)-Ethyl Tetrahydro-2-furanacetate (21): 0.51 g (3.2 mmol, 64%); scale-up (20x) gave 11.6 g (73.7 mmol, 74%), bp 56-58°C (2 mmHg), lit.[22a] bp 94-96°C (17 mmHg); IR (thin film) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (m, 1 H), 4.16 (q, 2 H, J = 7.1 Hz), 3.88 (m, 1 H), 3.76 (m, 1 H), 2.60 (dd, 1 H, J = 15.1, 7.2 Hz), 2.45 (dd, 1 H, J = 15.1, 6.0 Hz), 2.09 (m, 1 H), 1.91 (m, 2 H), 1.58 (m, 1 H), 1.27 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.2, 75.2, 67.9, 60.4, 40.6, 31.2, 25.5, 14.1; HRMS *m/e* for $C_8H_{14}O_3$ (M^++1): calcd 159.1021, found 159.1018. Anal. Calcd for $C_8H_{14}O_3$: C, 60.76; H, 8.86. Found: C, 60.58; H, 8.81.

(±)-Ethyl Tetrahydro-3,3-dimethyl-2-furanacetate (22): 0.73 g (3.94 mmol, 79%); IR (thin film) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (q, 2 H, J = 7.2 Hz), 3.85 (m, 3 H), 2.37 (d, 2 H, J = 7.1 Hz), 1.77 (m, 2 H), 1.27 (t, 3 H, J = 7.2 Hz), 1.07 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.8, 82.9, 65.5, 60.4, 40.7, 40.3, 35.8, 25.1, 21.6, 14.0; HRMS *m/e* for $C_{10}H_{18}O_3$: calcd 186.1256, found 186.1250. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.52; H, 9.68. Found: C, 64.09; H, 9.58.

(±)-Ethyl 2-Oxaspiro[4.5]decane-1-acetate (23): 0.90 g (3.98 mmol, 80%); IR (thin film) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (q, 2 H, J = 7.2 Hz), 3.87 (m, 2 H), 3.80 (m, 1 H), 2.38 (d, 2 H, J = 7.1 Hz), 1.94 (m, 1 H), 1.80-1.55 (complex, 3 H), 1.50-1.09 (complex, 8 H), 1.27 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 172.0, 83.4, 65.6, 60.4, 44.5, 35.8, 35.1, 34.9, 30.4, 26.1, 23.5, 22.8, 14.0; HRMS *m/e* for $C_{13}H_{22}O_3$ (M^++1): calcd 227.1647, found 227.1645. Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.73. Found: C, 69.29; H, 9.87.

(±)-Ethyl Tetrahydro-2*H*-pyran-2-acetate (24): 0.59 g (3.41 mmol, 68%); scale-up (20x) gave 14.5 g (84.3 mmol, 84%), bp 65-66°C (2 mmHg),

lit.[18d] bp 88-90°C (6 mmHg); IR (thin film) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (q, 2 H, J = 7.1 Hz), 3.96 (d, 1 H, J = 11.7 Hz), 3.74 (m, 1 H), 3.46 (m, 1 H), 2.51 (dd, 1 H, J = 15.0, 7.8 Hz), 2.36 (dd, 1 H, J = 15.0, 5.2 Hz), 1.82 (m, 1 H), 1.67-1.25 (complex, 5 H), 1.26 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.3, 74.3, 68.4, 60.3, 41.7, 31.4, 25.6, 23.2, 14.1; HRMS *m/e* for $C_9H_{16}O_3$ (M^++1): calcd 173.1178, found 173.1179. Anal. Calcd for $C_9H_{16}O_3$: C, 62.79; H, 9.30. Found: C, 62.77; H, 9.28.

(±)-Ethyl Tetrahydro-4,4-dimethyl-2*H*-pyran-2-acetate (25): 0.93 g (4.11 mmol, 82%); IR (thin film) 1742, 1390, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (q, 2 H, J = 7.1 Hz), 3.89 (m, 1 H), 3.74 (m, 1 H), 3.61 (dt, 1 H, J = 12.3, 2.3 Hz), 2.47 (dd, 1 H, J = 15.0, 8.0 Hz), 2.32 (dd, 1 H, J = 15.0, 5.0 Hz), 1.47 (dt, 1 H, J = 13.2, 5.0 Hz), 1.37-1.13 (complex, 3 H), 1.26 (t, 3 H, J = 7.1 Hz), 1.03 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.4, 70.1, 64.3, 60.3, 44.5, 41.7, 38.3, 33.0, 28.8, 23.9, 14.1; HRMS *m/e* for $C_{11}H_{20}O_3$ (M^++1): calcd 201.1491, found 201.1492. Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.00; H, 10.00. Found: C, 65.70; H, 9.78.

(±)-Ethyl Tetrahydro-4,4-dimethyl-2-furanacetate (26): 0.65 g (3.51 mmol, 70%); IR (thin film) 1738, 1385, 1370, 1185, 1062 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.36 (m, 1 H), 4.08 (q, 2 H, J = 7.1 Hz), 3.46 (A of ABd, 1 H, J = 8.1 Hz), 3.40 (B of ABd, 1 H, J = 8.1 Hz), 2.56 (dd, 1 H, J = 15.3, 7.4 Hz), 2.40 (dd, J = 15.3, 5.9 Hz), 1.82 (dd, 1 H, J = 12.3, 6.7 Hz), 1.35 (dd, 1 H, J = 12.3, 8.9 Hz), 1.19 (t, 3 H, J = 7.1 Hz), 1.03 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.2, 80.0, 75.3, 60.4, 46.5, 41.2, 39.7, 26.6, 26.3, 14.1; HRMS *m/e* for $C_{10}H_{18}O_3$: calcd 186.1256, found 186.1252. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.52; H, 9.68. Found: C, 64.44; H, 9.59.

(±)-Ethyl Tetrahydro-5,5-dimethyl-2*H*-pyran-2-acetate (27): 0.85 g (4.25 mmol, 85%); IR (thin film) 1740, 1390, 1370, 1185, 1092 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (m, 2 H), 3.66 (m, 1 H), 3.45 (dd, 1 H, J = 11.1, 2.5 Hz), 3.18 (d, 1 H, J = 11.1 Hz), 2.55 (dd, 1 H, J = 15.1, 7.6 Hz), 2.40 (dd, 1 H, J = 15.1, 5.3 Hz), 1.56-1.30 (complex, 4 H), 1.25 (t, 3 H, J = 7.1 Hz), 1.01 (s, 3 H), 0.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.3, 78.2, 74.3, 60.3, 41.2, 36.4, 29.6, 27.7, 27.0, 23.3, 14.1; HRMS *m/e* for $C_{11}H_{20}O_3$: calcd 200.1412, found 200.1410. Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.00; H, 10.00. Found: C, 65.95; H, 9.97.

(±)-Methyl Tetrahydro-2-methyl-2-furanacetate (28): 0.71 g (4.50 mmol, 90%); IR (thin film) 1742, 1380, 1220, 1100, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (dt, 2 H, J = 6.5, 2.8 Hz), 3.68 (s, 3 H), 2.54 (d, 2 H, J = 1.8 Hz), 1.95 (m, 3 H), 1.76 (m, 1 H), 1.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.71, 80.6, 67.3, 51.3, 45.2, 36.7, 26.1, 25.7; HRMS *m/e* for $C_8H_{14}O_3$ (M^++1): calcd 159.1021, found 159.1021. Anal. Calcd for $C_8H_{14}O_3$: C, 60.75; H, 8.86. Found: C, 60.36; H, 8.95.

(±)-Ethyl 3-Ethoxy-8-hydroxyoctanoate (31). Treatment of 1.14 g (5.00 mmol) of ethyl (*E*)-8-acetyloxy-2-octenoate (**20**) with 6.00 mmol of NaOEt in abs EtOH as described above gave a complex mixture of products. Using 12.0 mmol of base (0.28 g of sodium dissolved in 15 mL of abs EtOH), an 87:13 (GC) mixture of ethyl 3-ethoxy-8-hydroxyoctanoate and **20** was obtained. Purification by PTLC using 50% ether in hexane afforded 0.83 g (3.57 mmol, 72%) of **31** as a colorless oil. IR (thin film) 3450, 1740, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.14 (q, 2 H, J = 7.2 Hz), 3.72 (quintet, 1 H, J = 6.1 Hz), 3.63 (t, 2 H, J = 6.5 Hz), 3.51 (q, 2 H, J = 7.2 Hz), 2.53 (dd, 1 H, J = 15.0, 7.2 Hz), 2.39 (dd, 1 H, J = 14.9, 5.6 Hz), 1.90 (bs, 1 H), 1.55 (m, 4 H), 1.38 (m, 4 H), 1.27 (t, 3 H, J = 7.2

Hz), 1.16 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 171.9, 75.9, 64.7, 62.6, 60.3, 40.0, 34.4, 32.5, 25.7, 24.9, 15.4, 14.1; HRMS *m/e* for $C_{12}H_{24}O_4$ (M^++1): calcd 233.1752, found 233.1749. Anal. Calcd for $C_{12}H_{24}O_4$: C, 62.08; H, 10.34. Found: C, 62.18; H, 10.46.

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